INFLUENCE OF THE Sr AND Mg ALLOYING ADDITIONS ON THE BONDING BETWEEN MATRIX AND REINFORCING PARTICLES IN THE AISI7Mg/SiC-Cg HYBRID COMPOSITE

The aim of the work was to perform adequate selection of the phase composition of the composite designated for permanent - mould casting air compressor pistons. The hybrid composites based on AlSi7Mg matrix alloy reinforced with mixture of silicon carbide (SiC) and glassy carbon (Cg) particles were fabricated by the stir casting method. It has been shown that the proper selection of chemical composition of matrix alloy and its modification by used magnesium and strontium additions gives possibility to obtain both the advantageous casting properties of composite suspensions as well as good bonding between particles reinforcements and matrix.

Keywords: hybrid aluminium composites, Mg and Sr modification, solidification, structure, permanent - mould casting

1. Introduction

Increasingly, the composite materials of aluminium matrix alloy are applied to the production of structural components and machine parts, such as slide bearings, brake discs, sleeves and pistons [1,2]. The strong interest in this kind of composite materials are result from a number of their creative properties, which can be designed by the proper selection of reinforcing components, chemical composition of aluminium matrix and technological parameters. In most theoretical and experimental studies the authors proves that the presence of the hard of ceramic reinforcement (i.e: SiC, Al2O3) has a beneficial effect on the properties of Al matrix alloy, particularly on its hardness, wear resistance, thermal conductivity and thermal expansion as well as on dimensional stability [3-6]. Unfortunately, at the same time increase wear and reducing the durability of cutting tools were observed [7-9]. Therefore, most of the new studies focus on the formation of structure and properties of hybrid composites [9-16]. Such composites (i.e: Al/SiC-Cg or Al/SiC-graphite) have better physical, mechanical and tribological properties than the composites, which are reinforced by only one type of reinforcements [12]. It has been shown that graphite particles may create a protective lubricating layer between two contact surfaces during sliding [11]. The possibility to obtain of lubrication effect is very important and useful from the point of view of the machining of the finished composite product. Moreover the new composite material designed for pistons must have the proper thermal expansion and conductivity, good thermal shock resistance, suitable of tribological properties, advantageous mechanical properties, in particular fatigue strength, appropriate hardness, low density and damping capacity [17]. For this purpose the proper selection of both the chemical composition of the matrix and the type, size and volume fraction of reinforcing phase and more over the selection of technological parameters are necessary.

For all casting processes the aluminium matrix alloy should characterized high strength, possibility to heat treatment and good technological properties, such as a high castability, low viscosity and first of all good wettability on ceramic surface reinforcement. The poor wetting and reactivity between liquid Al alloy and ceramic particles such as silicon carbide (SiC), graphite (GR) and glassy carbon (Cg) are primary problems during the production of composite suspensions [14-21]. The wetting conditions can be improved by addition of proper alloying elements to the liquid aluminium alloy, the adequate preparing of surface reinforcement particles as well as through decreasing temperature and shortening the time of technological process.

In several studies have been shown that strontium (Sr) added to Al-Si casting alloys in order to change silicon crystals morphology what causes increases mechanical properties of the casts [22-24]. Razaghia et al. [24] demonstrated that the Sr addition has improved tensile strength and elongation in Al-Si matrix composites containing SiC and Al2O3 particles. They found that this could be attributed to the silicon crystal modification and wettability improvement of particle-matrix interface. As was shown the Sr segregates on both the silicon carbide and alumina particles and promotes the formation of an Al–Si–Sr intermetallic compound on the particle-matrix interface. Many authors described the significant role of magnesium (Mg) during the synthesis of the Al-Si matrix composites via the liquid processing [15,16,23,25,26]. It has been shown that addition of Mg into liquid Al alloy reduces its surface tension, prevents rejection of the particles from the melt and assists reaction-aided wetting. In own studies, concerning the CF/Al-MMC composites have been demonstrated that the introduction of alloying elements such as Mg and Sr into aluminium alloys is important not only from the point of view...
of proper wetting, but also for technological requirements [27]. The research showed decrease in solidification time and solidification temperature of alloys, which is important to the reactivity of Al/C, Al/GR and Al/SiC systems [15,27].

In this paper the effect of magnesium and strontium additions on aluminium matrix (AlSi7Mg) and AlSi7Mg/SiC-Cg hybrid composite microstructure designated for pistons have been presented.

2. Experimental procedures and methodology

The EN AC-AlSi7Mg alloy was applied as initial. Selection of aluminium alloy with 7% wt. silicon content provides reactivity reduction and decrease potential to forming the brittle carbide phases, i.e. Al₄C₃ in contact with SiC and Cg particles [16,20]. In the next step its refining and modification was performed. The procedure developed by the authors [28] include a step of removing the solid inclusions and hydrogen, refining initial alloy through the argon (Ar) blowing, and modify the initial chemical composition of the AlSi7Mg alloy. 30 minutes Ar refining takes place by barbotage with a stirrer, which through the gas flows in an amount of 1 dm³/h. Then, after removal from the molten metal a slag layer, the chemical composition of alloy were modified by the addition of Mg and Sr. The AlMg25 master alloy was used to increase the volume of Mg to 2% wt., while AlSr10 master alloy was used for the enrichment of the composition up to 0.03% wt. Sr. In order to homogenize its chemical composition, the alloy was stirred under reduced pressure (500 hPa) for another 30 min. This treatment modifies the surface tension at the liquid metal and improves wetting conditions of the ceramics. Into thus prepared matrix alloy were introduced the mixture of hybrid particles (5% wt. SiC and 2% wt. Cg). The next step in the preparation of the composite suspension based on a stir-casting. On the surface of the rotating liquid aluminium alloy was poured pre-heating the ceramic particles. After the introduction of the particles the composite suspension was homogenized (2 hours) and degassed under reduced pressure (500 hPa) and then casted into Quick-Cup mould for registration changes in temperature during the cooling. In the studies used a measuring system consisting of a recorder Spider 8, which enables registration of measurement data at a frequency of 50 Hz and standardized sensors sand QC4080 with thermocouple type K. Casting was done with the overheating of the alloy to a temperature of 720 °C. Based on data obtained in time of registration temperature changes during the cooling of castings in standard conditions determined the effect of modifying additives on solidification matrix alloy and composite material. The recorded data allowed to determine the cooling curves casting, the cooling rate curves (dT/dt) and reverse curves cooling rate (dt/dT). Based on the analysis of the characteristic points in cooling curves assigned the beginning and end of the solidification process of matrix alloy and the composite.

The analysis of chemical composition for alloys was performed using CCD arc-spark spectrometer (Foundry Master). The alloy composition was examined before and after modification. On the basis of calculations in the Thermo-Calc TCW5 (database TTAl7) indicates probable phase from the Al-Si-Mg-Sr that may be created under solidification matrix alloy with the chemical composition.

The structure of aluminium alloy and composite was examined using a light microscope (Olympus GX71) and scanning electron microscope (SEM). The structure of the particle/matrix boundaries was examined for the two types of particles using a high-resolution scanning electron microscope (HR SEM) with an attachment for the chemical analysis in micro-regions (EDS).

3. Results and discussions

The chemical composition of aluminium alloys according to supplier attestation* and based on the results obtained in tests using the mass spectrometer (Foundry Master) were showed in Tab 1.

In the graphs (Fig. 1-2) are marked characteristic points corresponding to a temperature of formation phases in the base AlSi7Mg alloy and after the modification with addition of 2% wt. Mg and 0.03% wt. strontium. On cooling curve for composite has also been marked characteristic points for the modified matrix alloy (Fig. 3).

![Fig. 1. The cooling curve of AlSi7Mg base alloy](image)

TABLE 1

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi7Mg*</td>
<td>bal.</td>
<td>6.58</td>
<td>0.72</td>
<td>0.08</td>
<td>0.22</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>AlSi7Mg**</td>
<td>93.7</td>
<td>5.03</td>
<td>0.429</td>
<td>0.0116</td>
<td>0.22</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>AlSi7Mg***</td>
<td>91.6</td>
<td>4.81</td>
<td>0.480</td>
<td>0.0107</td>
<td>0.134</td>
<td>3.78</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

* Alloy composition according to supplier attestation
** Alloy composition tested by using the mass spectrometer (Foundry Master)
*** Alloy composition after modification by Mg and Sr tested by using the mass spectrometer (Foundry Master)
The Fig. 1 shows the cooling curve of AlSi7Mg base alloy. It has been registered pronounced effect recalescence and first stop and the temperature at 613°C (point 1 - beginning of the creation FCC phase Al composed with 98.93% wt. Al; 0.77% wt. Si; 0.118% wt. Mg; 0.078% wt. Mn; 0.008% wt. Fe). At the point 2 (604°C) start precipitate α - phase with Al-Fe-Mn-Si system (61.6% wt. Al; 16.4% wt. Fe; 13.67% wt. Mn and 8.28% wt. Si). At the point 3 at temperature 578°C additionally is formed Al-Fe-Si β phase (59.09% wt. Al; 27.2% wt. Fe and 13.68% wt. Si). Finally at the 565°C (point 4s) start precipitate phase with Al-Sr-Si system (27.2% wt. Al; 28.4% wt. Si and 44.3% wt. Sr) and silicon. The solidification process was completed after 268 seconds at a temperature of 565°C (4e).

Fig. 2. The cooling curve of AlSi7Mg alloy with addition of 2% wt. Mg and 0.03% wt. Sr

For the modified AlSi7Mg matrix alloy with addition of 2% wt. Mg and 0.03%wt. Sr (Fig. 2) the first stop of temperature was recorded at the 615 °C (the beginning of the creation of the FCC A1 phase: 98.75% wt. Al; 0.63% wt. Mg; 0.51% wt. Si and 0.09% wt. Mn). At temperature 607°C (point 2) start precipitate Al₄SrSi₂ phase (27.28% wt. Al; 28.4% wt. Si and 44.3% Sr), next at 604°C (point 3) α - phase with Al-Fe-Mn-Si system (61.8% wt. Al; 16.9% wt. Fe; 13.18% wt. Mn and 8.08% wt. Si.). At the point 4 (temperature 574°C) β - Al-Fe-Si phase is formed (59.09% wt. Al; 27.2% wt. Fe and 13.68% wt. Si). At temperature 564°C (point 5) start precipitate Al₈FeMg₃Si and Mg₂Si phases. Moreover it was observed that the introduction of modifying additives decreases the temperature of Si precipitation to the 557 °C (point 6s) and extend the solidification time to 312 seconds (point 6e). Decreases the temperature of solidification appears to be preferred for the wettability between the liquid metal and ceramic.

The introduction of ceramic particles into the matrix alloy changes the conditions of solidification (Fig. 3). The first stop temperature was recorded at 608 °C (point 1) and after 228 seconds was observed the end of solidification at 556 °C (point 4e). During solidification of composite suspension can be identified 3 characteristic points for the formation of phases in modified AlSi7Mg aluminium alloy. The point 1 shows the beginning of the creation of two phases: FCC A1 and Al₄SrSi₂. At temperature 604°C (point 2) starts formation of β-AlFeSi phase. At Point 3 (564°C) starts the precipitation of Al₈FeMg₃Si and Mg₂Si phases.

The optical micrographs of AlSi7Mg aluminium alloys in both modified and non-modified conditions have been presented on Figs. 4 and 5. The microstructural observations showed that the Sr addition changes the eutectic network of Al-Si. The morphology of eutectic silicon was changed from coarse flake/acinular (Fig. 4a) to finer fibrous/globular (Fig. 4b). Also intermetallic phases in particular enriched in iron, manganese, and magnesium in both alloys were identified. Presence of these phases correlates with chemical composition of the alloys. It was confirmed that strontium
addition changes the morphology of these phases. About this aspect was described in detail by Tillová et al. [29]. Moreover in un-modified alloy, when magnesium content was less than 0.4 wt % along the sides of eutectic Si were observed small dark particles of Mg2Si phase (Fig. 5a). In turn increasing the magnesium content up to 2 wt. % leads to formation of Mg2Si phase in the form of “Chinese script” (5b). The similar effect was observed by Samuel et al. [23].

Also results of SEM observation confirmed the presence of phases resulting from theoretical considerations. The morphology of selected phases in modified matrix alloy has been presented in Figure 6. In the area marked as the spot 1 the α - phase with Al-Fe-Mn-Si was identified. In spot 2 the Al3SrSi2 phase was detected. It was observed that the both phases precipitated on the α-Al dendrite boundary.

The main purpose of applied modification was not only the change of matrix alloy structure in the state after casting, but also changing the properties of the liquid metal matrix in contact with reinforcement. On the basis of the results of composite microstructure observations, a uniform distribution of the reinforcing phases (Fig. 7) and good bonding between aluminium matrix were confirmed (Figs. 8a and Figs. 9a).

The SEM+EDS analysis at the area in front of interface between AlSi7Mg aluminium alloy modified by 2% wt. Mg and 0.03% wt. Sr and particles (both SiC and Cg) showed an increase of Si, Sr and O, (Figs. 8b and 9b). In turn, within the interface the slight increase in Mg and O and also Al were observed. Increase the intensity of Mg in the presence of oxygen, silicon and strontium could indicate occurrence both magnesium oxide, magnesium silicide, precipitates containing strontium and/or different kind of complex compounds from Al-Mg-O, Al-Mg-O-Si or Al-Mg-O-Si-Sr systems. The EDS mapping results confirmed the presence some of this phases (Figs. 10,11). However, the observations of border areas between modified AlSi7Mg matrix and SiC particles compared to glassy carbon particles revealed a significant differences in their morphology and segregations, as can be seen in Figs. 8a and 10 as well as Figs. 9a and 11, respectively.
Two different kinds of interfaces between SiC particles, and modified Al matrix were detected and identified. The first one had regular, coherent and rather clean areas without any reaction products. In the second kind of interfaces the slight reaction between components was noted. Based on the results of EDS mapping (Fig. 10), the occurrence of magnesium oxide at the Al/SiC interface was confirmed. The performed preliminary TEM analysis showed (Fig. 12), that near the area of interface are also small precipitates containing Al, O and Mg. Probably it is MgAl₂O₄ favourable spinel. However, to confirm this assumption the further more advanced studies are necessary.

The formation of unwanted, brittle phases, such as Al₄C₃ and Mg₂Si at the analysed interfaces, what has been described by many authors [30-34], wasn’t noticed. This proves, that besides proper of Si-content in the Al matrix alloy described by the authors [35-38], both magnesium and strontium are useful to reduce reactivity in the Al/SiC and Al/Cg systems and have a positive effect on quality of connection between components. However, further work is needed both the thermodynamic analysis as well as structural characterization by using advanced techniques under high resolution in order to understand the effect of alloying additions (i.e. Sr and Mg) on morphology and microstructure of reactively formed interfaces.

4. Conclusion

In the preparation of composites by modified stir-casting (suspension) method [28] are important not only the selection of the type and the volume fraction of reinforcing phase, but mainly adequate preparation of the matrix alloy. It has been shown that the addition of Mg and Sr decreases the temperature of solidification, which is important from the point of view of liquid technology. In the liquid state, these additives leads to interruption of oxide film from the aluminium alloy surface and reduces surface tension.

The investigations of composite structure showed, that the introducing of Mg and Sr additives into the aluminium alloy promotes the formation of the useful phases at the interface between the ceramic particles and matrix, which confirms the beneficial effect of modifiers on wetting conditions between liquid metal and ceramics.
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